(12) UK Patent Application (19) GB (11) 2 053 712 A

(21) Application No **7824972**
(22) Date of filing **18 Jul 1979**
(43) Application published
 11 Feb 1981
(51) INT CL^3
  B01J 23/64 23/68 23/85
  C07C 2/76 11/04 15/04 //
  B01J 23/94 23/96
(52) Domestic classification
  B1E 1123 1126 1193 1204
  1206 1298 1315 1318 1342
  1343 1345 1351 1365 1401
  1421 1422 1475 1476 1500
  1513 1625 1634 1701 1709
  1714 1722 1724 1729 1732
  1811 CB
(56) Documents cited
  GB 1373280
  GB 1369745
  GB 1308542
(58) Field of search
  B1E
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(54) Regenerable catalysts and process for the conversion of relatively low molecular weight hydrocarbons to higher molecular weight hydrocarbons.

(57) Regenerable catalysts for the conversion and oligomerization of hydrocarbons, e.g. methane, to produce products containing ethylene and/or benzene, comprise (1) a Group VIII noble metal having an atomic number of 45 or greater, nickel, or Group I-B noble metal having an atomic number of 47 or greater; (2) a Group VI-B metal oxide which is capable of being reduced to a lower oxide, or admixture of metal oxides which includes one or more of such metal oxides; and, (3) magnesium, strontium or barium, composited with a spinel-coated refractory support, notably an inorganic oxide support, or calcium composited with a non-zinc containing spinel-coated refractory support; preferably alumina.

ERRATUM

SPECIFICATION NO 2053712A

Front page, heading (21) Application No. *for* 7824972 *read* 7924972

THE PATENT OFFICE
3 April 1981

Bas 82139/14

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SPECIFICATION

Process for the conversion of relatively low molecular weight hydrocarbons to higher molecular weight hydrocarbons, catalyst - reagents for such use in such process, and the regeneration thereof

5   It is the business of many refineries and chemical plants to obtain, process and upgrade relatively low value
hydrocarbons to more valuable feeds, or chemical raw materials. For example, methane, the simplest of the
saturated hydrocarbons, is often available in rather large quantities either as an undersirable by product in
admixture with other more valuble higher molecular weight hydrocarbons, or as a component of an off gas
10   from a process unit, or units. Though methane is useful in some chemical reactions, e.g., as a reactant in the   10
commercial product of methanol and formaldehyde, it is not as useful a chemical raw material as most of the
higher molecular weight hydrocarbons. For this reason process streams which contain methane are usually
burned as fuel.
        Methane is also the principal component of natural gas, which is composed of an admixture of normally
15   gaseous hydrocarbons ranging C_4 and lighter and consists principally of methane admixed with ethane,   15
propane, butane and other saturated, and some unsaturated hydrocarbons. Natural gas is produced in
considerable quantities in oil and gas fields, often at remote locations and in difficult terrains, e.g., off-shore
sites, arctic sites, swamps, deserts and the like. Under such circumstances the natural gas is often flared
while the oil is recovered, or the gas is shut in, if the field is too remote for the gas to be recovered on a
20   commercial basis. The construction of pipelines to carry the gas is often not economical, due particularly to   20
the costs of connecting numerous well sites with a main line. Transport of natural gas under such
circumstances is also uneconomical because methane at atmospheric pressure boils at -258°F and
transportation economics distate that the gas be liquefiable at substantially atmospheric pressures to reduce
its volume. Even though natural gas contains components higher boiling than methane, and such mixtures
25   can be liquefied at somewhat higher temperatures than pure methane, the temperatures required for   25
condensation of the admixture is nonetheless too low for natural gas to be liquefied and shipped
economically. Under these circumstances the natural gas, or methane, is not even of sufficient value for use
as fuel, and it is wasted.
        The though of utilizing methane from these sources, particularly avoiding the tremendous and absolute
30   waste of a natural resource in this manner, has challenged many minds but has produced few solutions. It is   30
highly desirable to convert mthane to hydrocarbons of higher molecular weight than methane (hereinafter,
C_2^+) particularly admixtures of C_2^+ hydrocarbon products which can be economically liquified at remote
sites; especially admixtures of C_2^+ hydrocarbons rich in ethylene or benzene, or both. Ethylene and benzene
are known to be particularly valuable chemical raw materials for use in the petroleum, petrochemical,
35   pharmaceutical, plastics and heavy chemicals industries. Ethylene is thus useful for the production of ethyl   35
and ethylene compounds including ethyl alcohol, ethyl ethers, ethylbenzene, styrene, ethylene oxide,
ethylene dichloride, ethylene dibromide, acetic acid, polyethylene and the like. Benzene is useful in the
production of ethylbenzene, styrene, and numerous other alkyl aromatics which are suitable as chemical and
pharmaceutical intermediates, or suitable in themselves as end products, e.g., as solvents or high octane
40   gasoline components.   40
        It is a primary objective of the present invention to provide the art with novel catalysts, and a catalyst
process for the production of higher molecular weight hydrocarbons from lower moelcular weight
hydrocarbons, especially for the production of C_2^+ hydrocarbons from methane, natural gas, process
streams rich in methane, and the like.
45   A specific object is to provide novel regenerable catalyst-reagents, and a new and improved process   45
utilizing said regenerable catalyst-reagents, for the conversion, and oligomerization of methane at relatively
low temperatures to higher molecular weight hydrocarbons, particularly products rich in ethylene or
benzene, or both, usually in admixture with other hydrocarbons.
        These and other objects are achieved in accordance with the present invention which embodies:
50   (a)   novel multi-functional regenerable catalyst-reagents which are comprised of (1) a Group VIII noble   50
metal having an atomic number of 45 or greater, nickel, or a Group I-B noble metal having an atomic number
of 47 or greater (Periodic Table of the Elements; Sargent Welch Scientific Company, Copyright 1968), or
admixture which includes one or more of said metals; (2) a Group VI-B metal oxide of the Periodic Table of
the Elements which is capable of being reduced to a lower oxide, or admixture of metal oxides which
55   includes one or more of such metal oxides; and, additionally (3) selected from the group consisting of   55
barium, magnesium, strontium or an admixture which includes one or more of such metals, composited
with a suitably passivated, spinel-coated refractory support, notably an inorganic oxide support, preferably
alumina; or calcium, composited with a suitbly passivated, non-zinc containing spinel coated refractory
support, notably an inorganic oxide support, preferably alumina; ·
60   (b)   a novel hydrocarbon conversion process wherein a hydrocarbon feed, notably methane, or   60
methane-containing gas, is contacted with a catalyst-reagent as characterized in (a), supra, at temperature
ranging from about 1150°F to about 1600°F, preferably from about 1250°F, to about 1350°F at
sub-atmosphere, or supra atmospheric pressure sufficient to react and form C_2^+ hydrocarbons; and
        (c)   a process for regeneration of said catalyst-reagent which has become inactivated as by use in the
65   process characterized in (b), supra, by contact thereof in an exothermic reaction with water, oxygen or an   65

oxygen-containing gas, preferably air, at temperatures sufficient to reoxidize the Group VI-B metal oxide, or metal oxides, and preferably also sufficient to provide the required sensible heat to said novel hydrocarbon conversion process (b), supra on recycle of the catalyst-reagent; which suitably ranges from about 100°F, to about 1600°F, preferably from about 1250°F to about 1450°F, carbon dioxide and water being released in the
5   regeneration reaction.

The novel catalyst-reagents are multi-functional and, though the exact nature of the reaction paths are by no means certain, the included components are believed to play different mechanistic functions in the production of oligomers from the low molecular weight hydrocarbon feeds, notably methane. The Group I-B (silver, gold) or VIII (rhodium, palladium, osmium, iridium and platinum) noble metals, or nickel, the first
10   essential component, of which the Group VII noble metals notably platinum, iridium and palladium, but particularly platinum, are preferred, is believed to enter into a dissociative chemisorption reaction with the hydrocarbon feed and cause it to lose hydrogen. For example, in the reaction with methane, the Group I-B, Group VIII noble metal, or nickel, functions to cause dissociative chemisorption of the methane onto the surface of the catalyst to produce species which can react to form ethylene directly, another species which
15   reacts to form ethane and higher molecular weight aliphatic hydrocarbons, or both, and other species which can directly react with the Group VI-B metal oxide to form water.

The Group VI-B metal oxide, the second essential component, is characterized as an oxide which is capable of being reduced in the reaction to a lower oxide or the zero valent metal, or both. The reducible Group VI-B metal oxide component, comprising an oxide, or oxides, of the multivalent metals chromium,
20   molybdenum and tungsten, is believed to provide a catalytic function, in addition to the reagent function which is a function of the change of oxidation state of the metal. Thus, it acts as a reagent in that it is believed to donate oxygen for reaction with abstracted hydrogen to form water and thereby provide the energy necessary to sustain the reaction. In its catalytic function, it is believed that the low valence oxides of the Group VI-B metal, or the completely reduced metal, provide a cyclization function whereby acetylene,
25   acetylides and the like, and perhaps even ethylene are converted into aromatics, notably benzene. Thus, it is one or more of the products of the reagent function of the Group VI-B metal oxide components which are believed to provide the catalytic function of the Group VI-B metals.

It has also been found that the activity of the Group VI-B reducible metal oxide to react with abstracted hydrogen and form water can be supplemented, or enhanced, by the additional presence of oxides of (i)
30   Group III-A metals having an atomic number of 31 or greater (gallium, indium and thallium), (ii) Group IV-B transition metals of atomic number ranging from 22 to 40 (titanium and zirconium), (iii) Group V-B transition metals (vanadium, niobium and tan-talum), (iv) Group VII-B transition metals (manganese and rhenium), Group VIII non-noble metals of atomic number ranging from 26 to 27 (iron and cobalt), (vi) metals of the lanthanum series of atomic number ranging from 58 to 71 (cerium, praseodymium, neodynium, samarium,
35   europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium), and (vii) metals of the actinium series of atomic number ranging from 90 to 92 (thorium and uranium. Of these , the preferred oxygen donor compounds comprise the oxides of vanadium, niobium, rhenium, cerium and uranium.

The Group II-A metals (magnesium, calcium, strontium and barium,) of which barium is highly preferred,
40   constitute the third essential component of the catalyst. The Group II-A metal is put on the catalyst support as an oxide and, in performing its function, is believed to form a Group II-A metal carbide, or carbides as intermediates during the course of the reaction. This, of course, does not suggest that other species containing the Group II-A metal are not formed, and possibly active during the reaction. However, in an initial stage it is believed that the oxide of the Group II-A metal supplies oxygen which reacts with abstracted
45   hydrogen to form water, thus providing some of the energy for the reaction. Barium particularly as barium peroxide (BaO_2) ab initio, is believed to function particularly well in this aspect. The Group II-A metal carbides, particularly carbides of the heavier Group II-A metals, are also believed to form compounds which possess carbon-carbon bonds, or polycarbon-carbides which are through to be intermediates, or precursors of intermediates, in the formation of cyclic compounds. While most of these polycarbon-carbides are
50   believed to be C_2 species, making barium, in particular is believed to form some C_3 species, making barium especially preferred for generation of cyclic hydrocarbons by the present process.

It is also essential in the formation of these catalysts that the several components be composited with a passivated surface, spinel-coated inorganic metal oxide support, preferably a spinel-coated alumina upon which the several components are sequentially impregnated, or co-impregnated by any of the common
55   techniques in use for the preparation of heterogeneous catalysts. The term "spinel", as used herein, designats a binary oxide which is characterized as having either a normal or inverse spinel structure. The normal spinel structure can be represented by the formula MY_2O_4 wherein M and Y are cations of different metals, and inverse spinel structure can be represented by the formula $Y(XY)O_4$ wherein Y and X are cations of different metals. The sum of the cationic charges of a spinel, whether normal or inverse, is equal to 8. A
60   description of the spinel-type structures is found in *Structural Inorganic Chemistry*, A.F. Wells, 3rd Edition, Oxford, the Clarendon Press, 1962, at pages 487-488, herewith incorporated by reference.
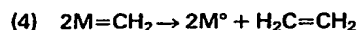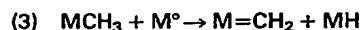
While calcium is the preferred Group II-A reagent metal it is nonetheless essential that calcium reagent not be employed in the presence of zinc. This is true even when the zinc is present as a constituent or part of the passivated, spinel-coated surface, e.g., as when the calcium is deposited on a zinc aluminate spinel carrier,
65   or zinc aluminate spinel coated support. The presence of zinc, among other things causes the formation of

considerable amounts of coke with drastic reduction in the formation of the desired products.
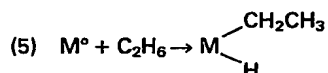
Thermodynamic considerations of the possible reaction paths favor the formation of a considerable amount of coke and/or carbon dioxide, with little or no yield of potentially valuable products, a conclusion which fits well with the results of many past experiments. However, pursuant to the practice of this
5 invention, albeit some coke, polymeric, or carbonaceous material is produced, essentially all of this material   5
that is formed in the reaction is burned to carbon dioxide and fully utilized in the regeneration stage to provide process heat. On the other side of the process, relatively little carbon dioxide is formed in the reactions taking place in the main reactor. It has been demonstrated that the catalyst-reagents of this invention, under the desired conditions for conducting the process, produce products containing an
10 admixture of valuable oligomers, particularly ethylene and benzene.   10

Though the exact nature of the reaction paths if by no means certain, as suggested, it is believed that the Group I-B noble metals and Group VIII noble metals, inclusive of nickel, function to cause one or more dissociative chemisorptions of the methane onto the surface of the catalyst to produce species which may react to form ethylene directly, or another species which may react to form ethance and higher molecular
15 weight aliphatic hydrocarbons, or both, and another species such as adsorbed hydrogen, which may react   15
directly with the transition metal or other oxide to form water. Or such species may react with the Group II-A carbides to liberate ethylene, form acetylene, or other products, form intermediates which lead to cyclization, or react with cyclization or polymerization products to form benzene or other products which appear in the exit gases from the reactor. The group VI-B metal oxide also may react directly with abstracted
20 or liberated hydrogen to form water, and by interaction with a Group I-B noble metal or Group VIII noble   20
metal, or nickel, is believed to form water and a species which further reacts to form ethylene. Where methane is used as a feed, it is thus envisioned that the reaction mechanisms with a mutlivalent Group I-B noble metal or Group VIII noble metal, or nickel, referred to as "M", may include the following sequences of reactions, to wit:
25   25

$$(1) \quad M° + CH_4 \rightarrow M\!\!\begin{array}{c} \diagup CH_3 \\ \diagdown H \end{array} \rightarrow MH + MCH_3$$

30          $(2) \quad 2MCH_3 \rightarrow 2M° + H_3C-CH_3$ 30

$(3) \quad MCH_3 + M° \rightarrow M=CH_2 + MH$

$(4) \quad 2M=CH_2 \rightarrow 2M° + H_2C=CH_2$
35   35
and,

$$(5) \quad M° + C_2H_6 \rightarrow M\!\!\begin{array}{c} \diagup CH_2CH_3 \\ \diagdown H \end{array}$$
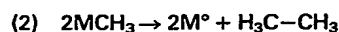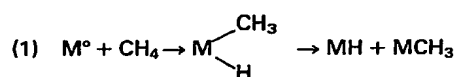
40   40
It is also envisioned that the multivalent transition metal oxide, $M'O_n$, the transition metal being designated as M', the oxygen atoms associated with M', or the ratio of oxygen atoms to M atoms in the association since n need not be an integer, reacts with the intermediate MH [Equation (1), supra] as follows:

45          $(6) \quad 2MH + M'O_n \rightarrow M° + M'O_{n-1} + H_2O$ 45
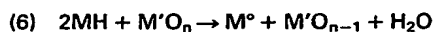
and with abstracted and liberated hydrogen as follow;
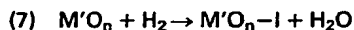
$(7) \quad M'O_n + H_2 \rightarrow M'O_n - l + H_2O$
50 and, M' participates with M in reacting with methane, as follows: 50

$(8) \quad M'O_n + CH_4 + M° \rightarrow M'O_{n-1} + H_2O + M=CH_2$
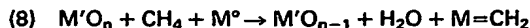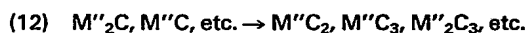
Likewise, MO_{n-l} and $M'O_{n-l}$ can further react in similar manner to produce additional water, ethylene,
55 ethane, and other hydrocarbons until the valance of M, M' and M" have been reduced to some lower level or   55
to zero, at which time further reactions such as described are no longer possible without reoxidation of the catalyst by regeneration.

The presence of the Group II-A metal component, favors the production of larger amounts of benzene in the products of the reaction. In this type of reaction, it is believed that the methane or organometallic
60 intermediates interact with the Group II-A metal component to form metal carbides and water. The carbides,   60
acetylides, propadiynides and the like, it is believed, react in turn with the water or abstracted or liberated hydrogen to generate benzene, ethylene, and/or the other products of the process.

It is known that acetylene can be trimerized at certain conditions to yield benzene, but it is also known that free acetylene also has a propensity to react to form coke; which form of reacting is high undesirable. Such
65 reaction can thus be represented by the following equation, to wit: 65

$$(9) \quad C_2H_2 \rightarrow Heat + (C_2)_x + H_2 \text{ (or Coke } + H_2)$$

In the catalytic reaction of this invention, however, it is not believed that free acetylene is formed and whereinafter C_2H_2 is represented in the equation, the acetylene is believed present only as a transient, or molecular species complexed with one or more metal atoms, and which is rapidly converted into benzene, ethylene or other hydrocarbon or coke. Therefore, it is theorized that the reaction pathway to the formation of benzene may be shown by equations 10-16, infra. Representing Group II-A metals as M''', and a carbide, acetylide, or the like of such metals as M'''_mC, M'''_mC_2, M'''_mC_3, the designations denoting the degree of association of carbon/carbide anions within the material, all of which generally fit in the "metal carbide" category, and the subscripts denoting generally the number of metal atoms associated with each carbide anion carbon or group of carbons, the following reactions are believed to occur informing the carbides, acetylides, to wit:
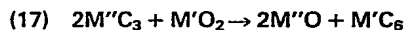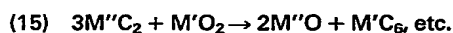
$$(10) \quad 2M''O + CH_4 \rightarrow M''_2C + 2H_2O$$

$$(11) \quad M''O_2 + CH_4 \rightarrow M''C + 2H_2O$$

$$(12) \quad M''_2C, M''C, \text{ etc.} \rightarrow M''C_2, M''C_3, M''_2C_3, \text{ etc.}$$

The acetylene forming reaction is represented by the following equation, to wit:

$$(13) \quad M''C_2 + H_2O \rightarrow M''O + C_2H_2$$
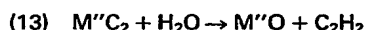
The acetylene trimerization may be represented by the following equation:

$$(14) \quad 3C_2H_2 + Catalyst \rightarrow C_6H_6 + Catalyst$$
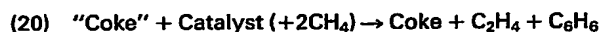
Where the catalyst is M'^o or lower valent $M'O_z$ and a similar sort of dimerization of C_3 materials is likewise possible. An alternate more likely cyclization route can also take place directly from the carbide, to wit:

$$(15) \quad 3M''C_2 + M'O_2 \rightarrow 2M''O + M'C_6, \text{ etc.}$$

$$(16) \quad M'C_6 + 6MH \rightarrow 6M^o + C_6H_6$$

$$(17) \quad 2M''C_3 + M'O_2 \rightarrow 2M''O + M'C_6$$

$$(18) \quad M'C_6 + 6CH_4 + 6M^o \rightarrow M' + 6MCH_3 + C_6H_6$$

Another alternate pathway for the cyclization to benzene involves the dehydrogenation and cyclization of three ethylenes via ractions on the M and M' catalyst and reagent metals.

However, it is also possible that the reaction pathway to C_2^+ hydrocarbons, inclusive of ethylene and benzene may be through the catalytic or thermal formation of a particular type of "coke" which catalytically or thermally decomposes in the reaction to form the thermally stable volatile products, benzene and ethylene, to wit:

$$(19) \quad CH_4 + Catalyst \rightarrow \text{"Coke"} + Catalyst + H_2O$$

$$(20) \quad \text{"Coke"} + Catalyst (+2CH_4) \rightarrow Coke + C_2H_4 + C_6H_6$$

The catalyst or feed, or both, may be furnishing hydrogen to decompose the "Coke" as, to wit:

$$(21) \quad M^o + CH_4 \rightarrow MH + \text{"Coke"}$$

$$(22) \quad MH + \text{"Coke"} \rightarrow M^o + C_2H_4 + C_6H_6$$
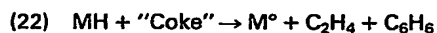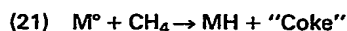
In the preparation of the catalyst-reagents, a porous metal oxide support, preferably one which has been desurfaced by contact with steam, is first passivated and the surface thereof converted to a spinel. This is accomplished by treatment of th support with at least one metal component, (other than zinc when calcium is to be deposited on the support), preferably a Group II-A metal, such that the sum of the ionic charges of the metal of the metal oxide support and the metallic element, or metallic elements, of the metal component used to treat the support satisfy the requirement for spinel formation, i.e., that the sum of the valences equals 8 and the ionic radii of the metals satisfy the requirements for formation of the normal or inverse spinel type structures. Exemplary of materials which can be used as supports are magnesium oxide, titanium oxide, zirconium oxide, hafnium oxide, and the like, preferably alumina. Suitably, the metal oxide support, preferably one having an initial surface area ranging from about 50 m^2/g to about 250 m^2/g,

preferably about 150 m²/g, is treated by contact, and impregnation with a solution of a compound of the desired metal component which is deposited on the metal oxide support. The treated or impregnated metal oxide is subsequently calcined, suitably at a temperature ranging from about 925°F to about 1825°F, this producing a surface spinel or spinel-coating on the metal oxide support. The spinel surfaced support is then
5 treated with a solution, or solutions, containing compounds which provide the essential substitutents   5
characterized in (a), supra.
     The several components are deposited on the passivated spinel-coated support by the impregnation method. Pursuant to this method, a compound, or compounds which contain the desired metal, or metals, are dissolved in solution in the desired concentration. The support in solvated, dry or calcined state is
10 contacted with the metal or metals-containing solution, or solutions, and thereby impregnated by either the   10
so-called "incipient wetness" technique, or technique embodying adsorption from a dilute solution, or solutions, with subsequent drying of the support. In the impregnation procedure, the Group II-A metal is generally first impregnated onto the passivated, spinel-coated support; the amount added to the support being additional to any such similar or dissimilar metal which may have been used to form the
15 spinel-coating, since that used in forming the spinel is not contained thereon in active form. The Group II-A   15
metal impregnated support is then, preferably, calcined in an inert or oxidizing atmosphere and the Group VI-B is then impregnated onto the support, and again calcined. Suitably, also, compounds of the Group II-A and VI-B metals can be coimpregnated onto the passivated, spinel-coated surface and the support then dried and calcined. It is essential, in either event, after deposition of the Group VI-B metal to calcine the
20 catalyst-reagent in an oxidizing atmosphere, i.e., in the presence of air or an oxygen-containing gas, to   20
convert the Group VI-B metal to an oxide. The Group III-A, and transition metals of IV-B, V-B, VII-B, inclusive also of the lanthanide and actinium series metals, and iron and cobalt, alone or in admixture with other metals are similarly impregnated onto the support and the impregnated support calcined in an oxidizing atmosphere to form an oxide, or oxides of the metal. The Group I-B or Group VIII noble metal, or nickel, is
25 generally impregnated onto the passivated, spinel-coated support after deposition of the other essential   25
components and then calcined, suitably in nitrogen; or added by coimpregnation with one or more of the other essential or non-essential components. Where the impregnating compound contains halogen, or other undesirable component, wet calcination may be employed to remove the halide from the catalyst-reagent. In all embodiments, the support can be treated by contact with a single solution containing the desired
30 amounts of a metal, or metals, or treated sequentially by contact with a solution containing one metal, and   30
then with a solution which contains another metal, or metals, in the desired amounts. Large particles, whether pilled, pelleted, beaded or extruded, can be so-treated and then crushed to the desired size, or the particle can be pre-reduced in size, and then treated. The catalyst-reagent, in either instance, can then be dried, calcined and then contacted as a fixed, fluidized or moving bed with the feed at the desired reaction
35 conditions.   35
     In the preparation of the catalyst-reagents, the Group I-B or Group VIII noble metals, or nickel, is deposited on the support in concentration ranging from about 0.01 percent to about 2 percent, preferably from about 0.1 to about 1 percent, calculated as metallic metal based on the weight of the total catalyst-reagent (dry basis). The reducable Group VI-B metal oxide is deposited on the catlyst-reagent in concentration sufficient
40 to supply at least one-half of an atom of oxygen for each hydrocarbon molecule which is to be oligomerized,   40
and preferably at least one atom of oxygen for each hydrocarbon which is to be oligomerized. Generally, at least bout 1.1:1 to at least 1.5:1 atoms of oxygen are supplied for each molecule of methane when high ethylene content is desired in the product. At lest 1.5:1 atoms of oxygen are supplied for each molecule of methane when high benzene content is desired in the product. The Group VI-B metal is deposited on the
45 catalyst-reagent in concentration ranging from about 1 percent to about 20 percent, preferably from about 3   45
percent to about 10 percent, calculated as metallic metal based on the weight of the total catalyst-reagent (dry basis). Suitably also the oxides of the Group III-A metals, the oxides of the Group IV-B, V-B, VII-B transitional metals, the oxides of iron, cobalt and the oxides of the metals of the lanthanide and actinide series are deposited on the catalyst in concentration ranging from about 0.01 percent to about 25 percent,
50 preferably from about 5 percent to about 15 percent calculated as metallic metal based on the weight of the   50
total catalyst-reagent (dry basis). The oxide of the Group II-A, or alkaline earth metal is deposited on the catalyst-reagent in concentration ranging from about 1 percent to about 30 percent, preferably from about 5 percent to about 25 percent calculated as metallic metal based on the weight of the total catalyst-reagent (dry basis). In compositing these metals with the catalyst-reagent, the Group II-A metal is composited in an
55 amount sufficient to provide an atomic ratio of at least about 3:1 relative to the Group VI-B metal, and   55
preferably the ratio of the Group II metal/Group VI-B metal ranges from about 3:1 to about 40:1, preferably from about 5:1 to about 12:1 when a relatively high concentration of benzene is desired in the product.
     The catalyst-reagent, particularly in view of its dual role as reagent and catalyst, eventually loses its activity and its activity must be restored. Restoration of the activity of the catalyst-reagent is performed by
60 oxidative regeneration, i.e., by contact of the catalyst-reagent with water, oxygen or oxygen-containing gas,   60
preferably air, at temperatures sufficiently elevated to burn off accumulated coke and reoxidize the Group VI-B metals and Group II-A metals; as well as the metals of Groups III-A, IV-B, VII-B, iron, cobalt and the lanthanides and actinides, to the extent they are present in the catalyst-reagent. Temperatures on the order of about 700°F are generally adequat to reoxidize these metals and restore the activity of the
65 catalyst-reagent, but preferably temperatures on the order of about 1000°F to about 1600°F, more preferably   65

from about 1250°F to about 1450°F, are employed in the regeneration zone and the hot regenerated
catalyst-reagent is recycled to the hydrocarbon reaction zone in quantity sufficient to supply the sensible
heat needed for the reaction. Generally, adequate heat is maintained by burning the coke from the
catalyst-reagent during the regeneration. Pressure, while not critical, is generally maintained above
5 atmospheric, suitably between atmospheric and about 20 atmospheres.   5
    The invention will be more fully understood by reference to the following non-limiting examples which
illustrate its more salient features. All parts are in terms of weight except as otherwise specified.

Example 1

10   A catalyst-reagent, Catalyst A, was prepared from a $MgAl_2O_4$ spinel blocked alumina support made by   10
impregnating via the incipient wetness technique a commercially available, high purity gamma alumina
calcined at 1000°F for two hours to product an alumina having a surface area of 193 m^2/g (B.E.T.) with an
aqueous solution of magnesium nitrate. The magnesium solution was added to the support in amount
calculated to deposit 2.9 percent Mg onto the support. The impregnated support was dried, and then
15 subjected to a subsequent calcination at 1000°F for four hours, and at 1300°F for an additional hour. The   15
$MgAl_2O_4$ spinel blocked alumina support was then impregnated with an aqueous barium nitrate solution and
calcined for 4 hours at 1000°F. The barium nitrate impregnation was also via the incipient wetness technique
with subsequent calcination, alternate impregnations and calcinations having been conducted nine times in
sequence to bring the barium concentration up to 6.9 percent. After the final calcination, a chromium nitrate
20 solution was then impregnated onto the catalyst-reagent to provide chromium concentration of 5.0 percent   20
after calcination for 4 hours at 1000°F with subsequent calcination in air at 1300°F for 1 hour. The calcined
catalyst-reagent was then impregnated by adsorption from dilute solution with a hexchloroplatinic acid,
H_2PtCl_4, solution sufficient to provide 0.3 weight percent platinum on the catalyst-reagent and again calcined
for 16 hours in air at 1300°F.

25   25
Example 2
    A 5 gram portion of Catalyst-reagent A was charged into a quartz tube furnace and heated slowly at
essentially ambient pressure with a flowing stream of nitrogen over a period of 6 hrs. to 1300°F. The flow of
nitrogen was then discontinued, and then a stream of essentially pure methane (99.4%) was passed across
30 the catalyst-reagent for 30 minutes. The flow of methane was then discontinued and nitrogen was again   30
introduced, the nitrogen having been substituted at the end of this period to act as a carrier gas. The entire
effluent was collected in a neoprene rubber bag during the time that hydrocarbons were evolved from the
system. A sample of the collected product was then subjected to a mass spectrometric gas analysis. The
following Table I shows the hydrocarbon components present in the gaseous product in significant quantity.
35   35

TABLE 1

Component	Mol Percent	Weight Percent
40 CH_4	55.480	39.441 40
C_2H_4	4.000	4.983
C_2H_6	1.634	2.178
C_4H_8	0.014	0.028
n-C_4H_{10}	0.001	0.002
45 C_6H_6	2.367	8.192 45

    The coke on the catalyst was measured at 1.04 wt.%, approximately 44.8 mole percent of the methane
having been converted with a maximum of 19.3 mole percent of the methane having formed coke; for a
significant amount of the coke is carbides which are capable of further conversion. Approximately 25.4 mole
50 percent of the methane was converted to C_2^+ product, 8 mole percent of the methane having formed   50
ethylene, 3.26 mole percent of the mathane having formed ethane, and 14.4 percent of the methane having
formed benzene.

Example 3
55   An additional series of catalysts, prepared as in Example 1, but with the impregnation of other essential   55
metallic or metal oxide components, or other blocking agent for preparation of the spinel; and these
catalysts employed in a series of runs at conditions similar to that described in Example 2. The results
obtained are tabulated in Table II.

TABLE II

Catalyst	A	B	B'	B''	C	D
Use	Original	Original	Regenerated[1]	Regenerated[2]	Original	Original
Base Material	γ-Al₂O₃	γ-Al₂O₃	γ-Al₂O₃	γ-Al₂O₃	γ-Al₂O₃	γ-Al₂O₃
Blocking Metal	Mg	Mg	Mg	Mg	Ba	Mg
Concentration Blocking Metal	2.9	3.7	3.7	3.7	4.3	4.1
Metal M	Pt	Pt	Pt	Pt	Pt/Ir	Pt/Ir
Concentration M (Wt. %)	0.3	0.1	0.1	0.1	0.1/0.1	0.1/0.1
Metal M'	Cr	Cr	Cr	Cr	W	Cr
Concentration M' (Wt. %)	5.0	3.9	3.9	3.9	9.5	5.4
Metal M''	Ba	Ba	Ba	Ba	Ba	Ba
Concentration M'' (Wt. %)	6.9	12.3	12.3	12.3	12.6	16.2
Metal M'''	–	V	V	V	U	U
Concentration M''' (Wt. %)	0.0	10.1	10.1	10.1	5.7	9.8
Product Analysis Component (Mole %)						
CH₄	55.58	44.33	45.72	42.69	51.30	36.71
C₂H₂	–	0.01	–	–	0.00	–
C₂H₄	4.00	3.54	3.95	3.02	5.68	2.53
C₂H₆	1.63	0.25	0.40	0.56	1.92	0.03
C₃H₆	–	–	0.01	–	0.02	–
C₃H₈	–	–	0.00	–	0.01	–
C₄H₈	0.01	0.64	0.01	0.00	–	–
n-C₄H₁₀	0.00	–	0.00	–	0.01	–
C₆H₆	2.37	3.89	3.56	3.67	1.84	3.95
N₂	Balance	Balance	Balance	Balance	Balance	Balance
Coke on Catalyst (Wt. %) [3]	1.04	9.56	0.78	1.13	1.57	0.34
Coke on Catalyst After Regeneration (Wt. %)	0.03	0.09	0.17	0.02	0.31	0.01

(1) B' is Catalyst B once regenerated.
(2) B'' is Catalyst B' once further regenerated.
(3) "Coke on Catalyst" may also include significant quantities of metal carbide "carbon".

Example 4

Catalyst-reagents were prepared from spinel blocked alumina supports made by impregnating via the incipient wetness technique a commercially available, high purity gamma alumina calcined at 1000°F for two hours to produce an alumina having a surface area of 193 m²/g (B.E.T.) with an aqueous solution of a salt of
5 the blocking metal. For example, in the preparation of a $CaAl_2O_4$ spinel blocked alumina support, a calcium   5
nitrate solution was formed by dissolving calcium nitrate in water, and the calcium solution was then added to the support in amount calculated to deposit 3.5 percent Ca onto the support. The impregnated support was dried, and then subjected to a subsequent calcination at 1000°F for four hours, and at 1300°F for an additional hour. The $CaAl_2O_4$ spinel blocked alumina support was then impregnated with an aqueous
10 solution of a salt of the desired Group II-A metal, e.g., calcium nitrate, as in the preparation of Catalyst F, and   10
calcined for 4 hours at 1000°F. Impregnation was also via the incipient wetness technique with subsequent calcination, alternate impregnations and calcinations having been conducted a number of times in sequence to bring the Group II-A metal concentration to the desired concentration. After the final calcination, a Group VI-B metal, Cr was deposited from a solution of a salt of the Group VI-B metal onto the catalyst-reagent to
15 provide the desired Group VI-B metal concentration after calcination for 4 hours at 1000°F with subsequent   15
calcination in air at 1300°F for 1 hour. The calcined catalyst-reagent was then impregnated by adsorption from dilute solution with an acid salt of the Group VIII noble metal, e.g., a hexachloroplatinic acid, H_2PtCl_4, solution sufficient to provide the desired concentration of platinum on the catalyst-reagent, and again calcined for 16 hours in air at 1300°F.
20   A 5 gram portion of each catalyst was charged into a quartz tube furnace and heated slowly at essentially   20
ambient pressure with a flowing stream of nitrogen over a period of 6 hrs. to 1300°F. The flow of nitrogen was then discontinued and then a stream of essentially pure methane (99.4%) was passed across the catalyst-reagent for 30 minutes. The flow of methane was then discontinued and nitrogen was again introduced the nitrogen having been subsituted at the end of this period to act as a carrier gas. The entire
25 effluent was collected in a neoprene rubber bag during the time that hydrocarbons were evolved from the   25
system. A sample of the collected product was then subjected to a mass spectrometric gas analysis to determine the hydrocarbon quantity, and the amount of coke deposited on the catalyst was measured.

The results obtained are given in Table III below

TABLE III

Testing of catalyst reagents for methane polymerization

	7	8	9	10
Test Run Number	7	8	9	10
Catalyst Designation	E	F	F₂	G
Nominal Catalyst Type	CaCrPt	CaCrPt	CaCrPt	CaMoVPt
Use	Original[2]	Original[1]	Regenerated[2]	Original[1]
Base Material M'''''_mO_n	$\gamma\text{-}Al_2O_3$	$\gamma\text{-}Al_2O_3$	$\gamma\text{-}Al_2O_3$	$\gamma\text{-}Al_2O_3$
Blocking Metal M''''	Zn	Ca[3]	Ca[3]	Ca[3]
Concentration Blocking Metal M'''' (Wt. %)	5.7	3.5	3.5	3.4
Metal M	Pt	Pt	Pt	Pt
Concentration M (Wt. %)	0.2	0.2	0.2	0.3
Metal M'	Cr	Cr	Cr	Mo
Concentration M' (Wt. %)	3.8	3.8	3.8	7.0
Metal M''	Ca	Ca	Ca	Ca
Concentration M'' (Wt. %)	8.3	8.3	8.3	9.2
Metal M'''	--	--	--	V
Concentration M''' (Wt. %)	0.0	0.0	0.0	10.2
Product Analysis **Component (Mole %)**				
CH_4	63.24	39.95	46.20	44.75
C_2H_2	--	--	--	0.03
C_2H_4	0.03	2.33	2.87	3.64
C_2H_6	0.16	0.38	0.46	0.19
C_3H_6	--	--	--	0.02
C_3H_8	--	0.01	--	0.00
C_4H_8	0.005	--	0.01	0.00
$n\text{-}C_4H_{10}$	0.01	--	0.02	0.01
C_6H_6	0.00	2.14	2.46	1.99
N_2	36.55	55.21	47.98	49.37
Product Composition **Component (Wt. %)**				
CH_4	49.61	26.34	31.23	30.34
C_2H_2	--	--	--	0.03
C_2H_4	0.04	2.69	3.39	4.32
C_2H_6	0.24	0.47	0.58	0.24
C_3H_6	--	--	--	0.04
C_3H_8	--	0.02	--	0.00
C_4H_8	0.01	--	0.02	0.01
$n\text{-}C_4H_{10}$	0.03	--	0.05	0.02
C_6H_6	0.00	6.87	8.10	6.57
N_2	50.07	63.60	56.63	58.44
Coke on Catalyst (Wt. %) [4]	28.73	2.48	2.16	1.74
Coke on Catalyst After Regeneration (Wt. %)[6]	0.24	0.11	0.22	0.16

(1) Original catalysts used in first cycle of methane polymerization.
(2) F₂ Catalyst F once regenerated, used in the second cycle of methan polymerization.
(3) Concentration of blocking reagent metal M'''' used for spinel formation is not included as part of M'' concentration even though the identical metal was used for both purposes.
(4) "Coke on Catalyst" may also include significant quantities of metal carbide "carbon".
(5) Testing at 1 atm, pressure, pure CH_4 feed, N_2 purge before and after, 0.5 hrs/run except first cycle on B above at 4.0 hrs.
(6) Regeneration by final 700°C air burning.

From these data it will be observed that catalysts which contain the Group II-A metal catalyst component, except where zinc is present (Test Run Number 7), are quite effective in oligomerizing methane to produce product compositions rich in ethylene and benzene. Where zinc is present, however, a major amount of the methane is converted to coke, with minimal production of C_2^+ gases.

It is apparent that various modifications and changes can be made without departing the spirit and scope

of the invention.

Temperatures expressed herein in °F are converted to °C by substracting 32 and then dividing by 1.8.

CLAIMS

1. A multi-functional regenerable catalyst-reagent composition suitable for the oligomerization of hydrocarbons, particularly methane, comprising (1) a Group VIII noble metal having an atomic number of 45 or greater, nickel, or a Group I-B noble metal having an atomic number of 47 or greater, (2) a Group VI-B metal oxide which is capable of being reduced to a lower oxide, and (3) a Group II-A metal selected from the Group consisting of barium, magnesium, strontium and an admixture which includes one or more such metals, composited with a spinel-coated refractory support, or calcium composited with a non-zinc containing spinel-coated refractory support.

2. A composition according to claim 1 in which the Group VIII noble metal is platinum, iridium or palladium.

3. A composition according to claim 1 or claim 2 in which the Group VI-B metal is chromium, molybdenum or tungsten.

4. A composition according to any one of claims 1-3 in which the spinel-coated inorganic oxide is alumina.

5. A composition according to any one of claims 1-4 additionally containing a Group III-A metal having an atomic number of 31 or greater, a IV-B, V-B or VII-B transition metal, iron, cobalt, or a metal of the actinide or lanthanide series.

6. A composition according to any one of claims 1-5 in which the said Group VIII noble metal or said Group I-B metal is present in a concentration in the range of from 0.01 percent to 2 percent, the said Group VI-B metal oxide is present in a concentration in the range of from 1 percent to 20 percent and said Group II-A metal is present in a concentration in the range of from 1 percent to 30 percent, said concentrations being calculated as metallic metal based on the total weight of the composition.

7. A composition according to any one of claims 1-6 in which the said Group II-A metal is present in an atomic ratio of at least 3:1 relative to the said Group VI-B metal.

8. A multi-functional regenerable catalyst-reagent composition according to any one of claims 1-7 substantially as hereinbefore described.

9. A composition according to claim 8 substantialy as hereinbefore described with reference to the Examples.

10. A process for the regeneration of th catalyst-reagent composition of any one of claims 1 to 9 which has become inactivated during use in a hydrocarbon conversion reaction comprising contacting said inactivated composition with water, oxygen or an oxygen-containing gas at a temperature in the range of from 1000°F (537.8°C) to 1600°F (871.1°C).

11. A regeneration process according to claim 10 substantially as hereinbefore described.

12. A process for the oligomerization of a hydrocarbon feed, preferably a methane containing-feed, comprising contacting said hydrocarbon feed with a catalyst-reagent composition of any one of claims 1 to 9 at a temperature in the range of from 1150°F (621.1°C) to 1600°F (871.1°C).

13. An oligomerization process according to claim 12 substantially as hereinbefore described.

14. Oligomers produced by the process of claims 12 or claim 13.